



Short communication

Effects of electrochemically active carbon and indium (III) oxide in negative plates on cycle performance of valve-regulated lead-acid batteries during high-rate partial-state-of-charge operation

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H I G H L I G H T S

- EAC in NAM prolongs the cycle life of VRLA batteries during HRPSoC operation.
- Appropriate addition of In_2O_3 in EAC can decrease the evolution rate of hydrogen.
- Appropriate addition of In_2O_3 and EAC in NAM can promote conversion of PbSO_4 to Pb.
- 0.02% In_2O_3 in NAM significantly prolongs the cycle life of VRLA batteries.

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In order to inhibit sulfation and hydrogen evolution of the negative plates and to prolong the cycle life of valve-regulated lead-acid batteries for hybrid-electric vehicles, electrochemically active carbon (EAC) and Indium (III) oxide (In_2O_3) are added into negative active materials of valve-regulated lead-acid batteries. The influences of EAC and In_2O_3 on the cycle performance of valve-regulated lead-acid batteries are investigated under high-rate partial-state-of-charge conditions. Experiment results indicate that addition of EAC in negative active materials can prolong the high-rate partial-state-of-charge cycle performance of valve-regulated lead-acid batteries, whilst it results in the accelerated evolution rate of hydrogen during charge process. It is also observed that EAC with an appropriate amount of In_2O_3 can effectively increase the overpotential of hydrogen evolution, which can not only produce the decreased hydrogen evolution rate and promote conversion of PbSO_4 to Pb in capacity recovery process, but also prolong the high-rate partial-state-of-charge cycle life of valve-regulated lead-acid batteries. The battery added with 0.5% EAC and 0.02% In_2O_3 in negative active materials exhibits at least four times longer cycle life than that without In_2O_3 .

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1. Introduction

Hybrid-electric vehicles (HEVs) require the battery to receive energy from regenerative braking and provide energy to start and accelerate the vehicles. The battery is charged and discharged at a very high frequency under high-rate partial-state-of-charge (HRPSoC) conditions. That means the charge and discharge process involves only a small fraction of the battery's capacity, but they occur continuously and do take place at a very high rate [1,2]. As a prospective candidate energy-storage system for HEVs

applications, valve-regulated lead-acid (VRLA) battery has advantages including low initial cost, well-established manufacturing base and distribution networks, and high recycling efficiency compared to other competitive technologies [3–5]. Nevertheless, the running cost of VRLA batteries is expensive because of its short service life. VRLA batteries fail prematurely due to the sulfation of the plates, particularly the negative plates [6,7]. The accumulation of lead sulfate reduces the effective reaction area of the negative plates, and makes the charge and discharge processes of the negative plates difficult [8].

Introduction of carbon materials to the negative plates of VRLA batteries could solve the problem of the sulfation of the negative plates. The use of carbon minimizes the uneven distribution of lead sulfate within the cross-section of negative plate, reduces discharge and charge current densities, and provides conductive network to

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facilitate subsequent charging process [9–11]. Nakamura et al. [9] found that the addition of carbon into the negative-active-mass (NAM) of VRLA batteries could restrain sulfation of Pb. Calabek [12] demonstrated that the presence of carbon in NAM could impede the continuous growth and deactivation of PbSO_4 crystals, improve the dispersion of the active substances, and enhance the utilization ratio of active substances. At the same time, carbon materials could supply double-layer capacitance during the processes of high rate charge and discharge or pulse discharge. It could also reduce the damage of the negative plates caused by providing high current density with buffer action, which is helpful for enhancing the cycle performance of the negative plates under HRPSoc conditions [6,13–15].

However, the introduction of carbon materials in the negative plates could produce the evolution of hydrogen in charging process, increase the inner pressure and accelerate water loss of battery, which negatively influences the life of battery. Therefore, it is necessary to reduce the hydrogen evolution rate on carbon materials in the process of charge. In this work, electrochemically active carbon (EAC) [11,16] and In_2O_3 were used as negative additives with the aim of inhibiting the hydrogen evolution on the negative plates and prolonging the cycle life of VRLA batteries under HRPSoc conditions.

2. Experimental

2.1. Preparation of negative plates

For the purpose of our investigation, two types of negative plates were prepared, namely, negative plates of EAC and negative plates of VRLA batteries. Negative plates of EAC were prepared by using EAC, acetylene black and different amounts of In_2O_3 . The content of acetylene black was 10%, and the content of In_2O_3 was varied from 0% to 8%. Negative plates of VRLA batteries were prepared by using lead oxide powder, barium sulfate, humic acids, and different amounts of EAC and In_2O_3 . The degree of oxidation of lead oxide powder was 76%. The contents of barium sulfate and humic acids were 1% and 0.3%, respectively. The content of EAC was varied from 0% to 2%, and the additive amounts of In_2O_3 were 0%, 0.005%, 0.01%, 0.02% and 0.04%, respectively.

2.2. Electrochemical measurements

Linear sweep voltammetric measurement was performed by a CHI430 electrochemical workstation. A prepared negative plate was used as the working electrode, a commercial PbO_2 positive plate was used as the counter electrode, and $\text{Hg}/\text{Hg}_2\text{SO}_4$ electrode was used as the reference electrode. The electrolyte was H_2SO_4 solution with a density of 1.347 g cm^{-3} . The scanning range was 0.00 to -1.50 V , and scanning rate was 5 mV s^{-1} .

The effects of In_2O_3 on the cycle performance of VRLA batteries under HRPSoc conditions were investigated by using 1.5 Ah cells. The thickness of the negative plate was 2 mm, while that of the positive plate was 2.5 mm. The electrolyte was H_2SO_4 solution with a density of 1.347 g cm^{-3} . Cycle performance under HRPSoc conditions was tested by using a BTS series battery testing system made by Neware Technology Limited. Firstly, the tested battery was discharged to 50% state-of-charge (SoC) at 1 C rate, then the charge/discharge cycle processes were carried out as follows: charge at 2 C rate for 60 s, rest for 60 s, discharge at 2 C rate for 60 s, rest for 60 s. The battery voltage was measured at the end of each charge and discharge processes, and the test process was stopped when the cut-off discharging voltage fell down to 1.60 V or when the cut-off charging voltage increased to 2.90 V.

2.3. Physical characterizations

The surface morphologies of the negative plates were examined at a voltage of 20 kV using a Hitachi S4700 scanning electron microscope. The crystalline phases of the negative plates were identified with a D/MAX-rB diffractometer ($\text{Cu K}\alpha$ radiation at 45 kV).

3. Results and discussion

3.1. Effects of EAC on cycle performance of VRLA batteries under HRPSoc conditions

The operation of VRLA batteries under HRPSoc conditions generates progressive accumulation of PbSO_4 on the negative plates, which leads to the short cycle life of VRLA batteries. The addition of EAC into the NAM can suppress the accumulation of PbSO_4 on the negative plates, and prolong the cycle life of VRLA batteries. Therefore in this study, different amounts of EAC were added into the NAM, respectively. Fig. 1 presents the effects of EAC on cycle performance of VRLA batteries under HRPSoc conditions. It can be seen that the addition of EAC into NAM could prolong cycle performance of VRLA batteries under HRPSoc conditions, and addition amount of EAC has great influence on the cycle life of VRLA batteries. The appropriate amount of EAC (0.5%) could increase HRPSoc cycle life of VRLA batteries 1.61 times longer than that one without EAC, whereas other addition amounts could not reach this level.

EAC additive can be adsorbed onto NAM surface, and enhance conductivity of the negative plates. EAC additive can also yield an electric double layer at the interface of carbon/solution, and increase the electrochemically active surface. The increased electrode surface sustains low electrode polarization, thus improves the charge efficiency of the negative electrode and increases the cycle life of VRLA batteries under HRPSoc conditions [11]. The accumulation of lead sulfate on the negative plates of VRLA batteries operated under HRPSoc conditions is one of the crucial factors responsible for the failure of VRLA batteries. EAC distributed in NAM contributes to the transfer of electrons to Pb^{2+} ions, and to the formation of Pb atoms. So EAC has a catalytic effect on the charge reactions and reduction of PbSO_4 proceeds via a parallel mechanism on both Pb and EAC surfaces, which retards the sulfation of the negative plates and prolongs the cycle life of VRLA batteries [16,17].

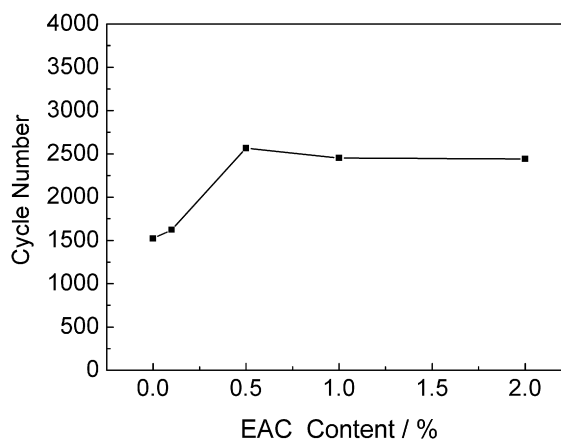


Fig. 1. Cycle performance of VRLA batteries added with different amounts of EAC in NAM under HRPSoc conditions.

3.2. Effects of In_2O_3 on the hydrogen evolution rate of EAC

The addition of EAC into NAM can restrain the sulfation of the negative plates [2,16], whereas it will lead to decrease of hydrogen evolution overpotential and increase of hydrogen evolution rate. As a result, the charge acceptance of the negative plates will decrease, and the inner pressure of VRLA batteries will increase. These effects all contribute to decreased cycle performance for VRLA batteries. In order to decrease the hydrogen evolution rate of EAC in H_2SO_4 solution, In_2O_3 was added into EAC. Fig. 2 shows the effect of addition amounts of In_2O_3 on the cathodic polarization curve of EAC in H_2SO_4 solution. The current peaks at the potential range of -1.16 to -1.18 V correspond to reduction of PbSO_4 to Pb [18]. It can be seen that the addition of In_2O_3 in EAC influences the hydrogen evolution overpotential and hydrogen evolution rate of EAC. With increasing In_2O_3 content in EAC, the hydrogen evolution rate decreased initially, and then increased; finally 4% In_2O_3 resulted in the minimum hydrogen evolution rate. It is well known that In_2O_3 is a kind of high hydrogen evolution overpotential material. In_2O_3 or In (III) ion can absorb on EAC surface in H_2SO_4 solution, suppress hydrogen evolution of EAC during cathodic polarization process. It is noteworthy that the addition amount of In_2O_3 in EAC should not be too much, otherwise the hydrogen evolution rate will be increased because of the negative catalysis of In_2O_3 [19].

3.3. Effect of In_2O_3 on cycle performance of VRLA batteries under HRPSoC conditions

Although carbon materials including EAC added into NAM of VRLA batteries inhibit accumulation of lead sulfate on the negative plates during HRPSoC duty, more hydrogen gas evolved on carbon materials results in terminating the charging process, which negatively affects the cycle performance of VRLA batteries [8]. Therefore some precautions must be taken to decrease or inhibit the hydrogen evolution on EAC in VRLA batteries. Based on the result given in Section 3.2, the different amounts of In_2O_3 (0%, 0.005%, 0.01%, 0.02% and 0.04%) together with 0.5% EAC were added into the NAM to prepare individual VRLA batteries. Firstly, In_2O_3 was fully mixed with EAC, and then the mixture was added into the NAM of VRLA batteries. After the formation process was finished, the HRPSoC cycle performance of VRLA batteries was tested.

Fig. 3 shows the cut-off charge/discharge voltages of the different VRLA batteries prepared during HRPSoC cycles, and Fig. 4 summarizes the effect of In_2O_3 on the HRPSoC cycle life of VRLA

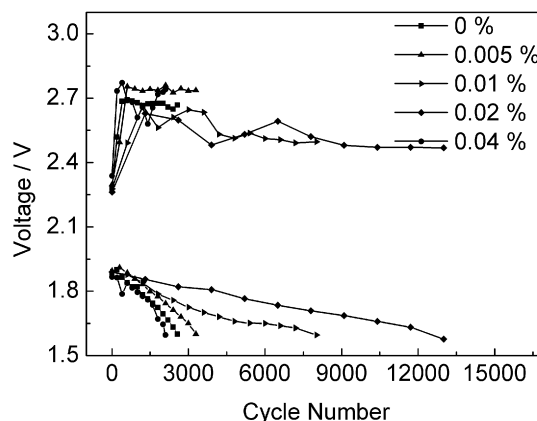


Fig. 3. Cut-off charge/discharge voltage of batteries contained different amounts of In_2O_3 in NAM during cycle test process.

batteries. In general, during HRPSoC cycle process, the cut-off voltage of VRLA batteries changed constantly. The cut-off charging voltage fluctuated, while the cut-off discharging voltage decreased gradually. When the cut-off charging voltage increased to 2.90 V or the cut-off discharging voltage decreased to 1.60 V, the cycle process was terminated automatically. In Fig. 3, the cut-off charging voltages of all batteries increased rapidly in the first five hundred cycles, and remained unchanged at a certain range thereafter. The cut-off discharging voltages of all batteries decreased gradually with increase of cycle number. It also can be seen from Fig. 3 that, although the cycle life of all batteries varied with the addition amounts of In_2O_3 in the negative plates, their cycle life termination reasons were same, i.e., the cut-off discharging voltages decreased to the lowest setting limit of voltage 1.60 V, while the cut-off charging voltages did not reach the highest setting limit of voltage 2.90 V. This phenomenon indicates that the content of In_2O_3 in the negative plates have a crucial influence on the charge acceptance of batteries. The amount of In_2O_3 added in the negative plate of every battery is different, so the ability of hydrogen evolution-restrain of every negative plate is different. That is to say that the charge acceptance of each battery is different. The cycle life of every battery is tested as follow: charge at 2 C rate for 60 s, and discharge at 2 C rate for 60 s. So the electric quantity of charge and discharge is equivalent for a battery in a single cycle. The battery with a higher charge acceptance could be charged more effective electric quantity, and it thus shows a higher cut-off discharging voltage at the end of the

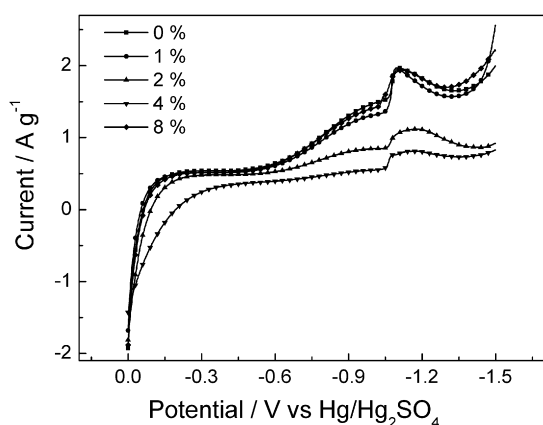


Fig. 2. Cathodic polarization curves of EAC contained different amounts of In_2O_3 at a scan rate of 5 mV s^{-1} .

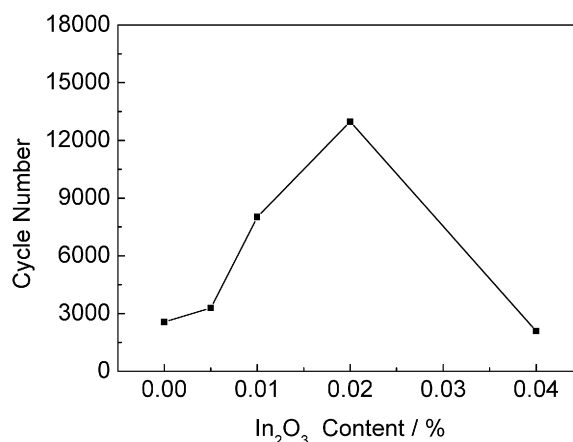


Fig. 4. Cycle life of VRLA batteries contained different amounts of In_2O_3 in NAM under HRPSoC conditions.

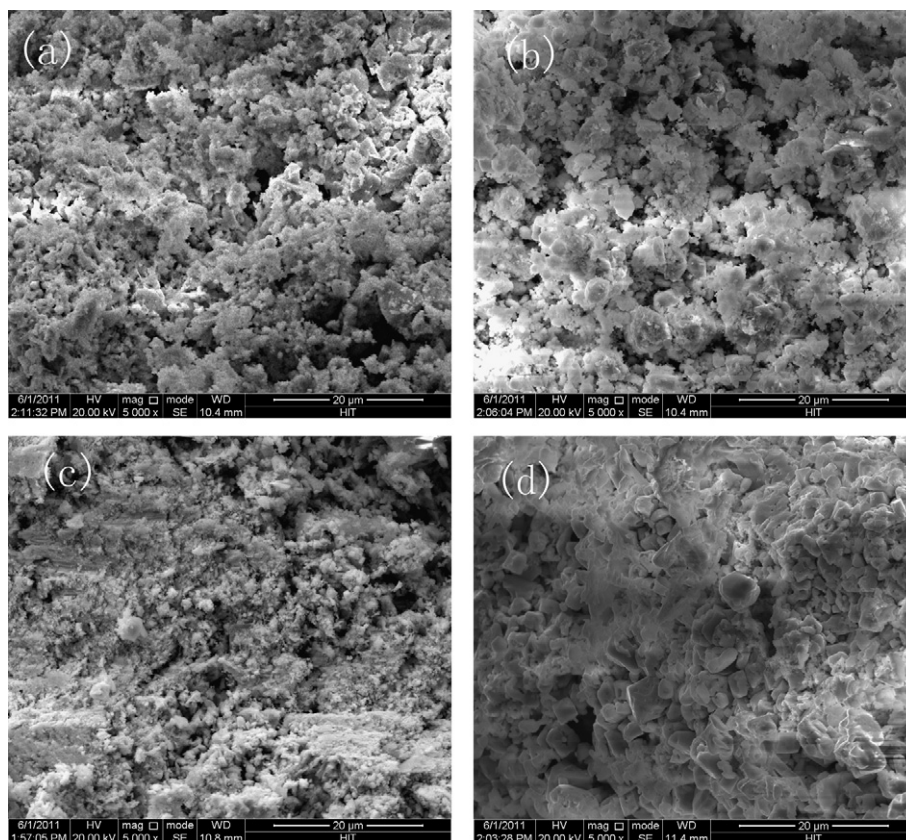


Fig. 5. SEM images of the negative plates containing (a) 0%, (b) 0.005%, (c) 0.02% and (d) 0.04% In₂O₃, the negative plates were fully recharged after cycle tests were finished.

discharge process. Therefore, it can be concluded that the battery with 0.02% In₂O₃ addition in NAM had a highest charge acceptance.

It can be found from Fig. 4 that, the cycle life of the batteries added with 0%, 0.005%, 0.01%, 0.02% and 0.04% In₂O₃ were 2564, 3292, 8011, 12,966 and 2095, respectively. With increasing In₂O₃ content, the cycle life of the battery increased initially, and then decreased. The battery containing 0.02% In₂O₃ in NAM, which corresponding to 4% In₂O₃ in EAC, had a maximum cycle life, five times more than the one without In₂O₃. The findings indicate that excessive In₂O₃ in NAM was harmful to HRPSoc cycle performance of VRLA batteries instead. Therefore it can be concluded that an appropriate amount of In₂O₃ in the negative plates can inhibit evolution of hydrogen during the charge process, and enhance the charge acceptance and HRPSoc cycle performance of the batteries.

3.4. Microstructures of the negative plates added with In₂O₃ after cycle test

In₂O₃ in the negative plate has a great influence on HRPSoc cycle performance of VRLA batteries. In order to well understand the effects of In₂O₃ on HRPSoc cycle performance of the battery, the surface morphology and composition of the negative plates added with different amounts of In₂O₃ were investigated. The negative plates were characterized by XRD and SEM after the batteries were fully recharged when termination of HRPSoc cycle tests. Fig. 5 presents SEM micrographs of the negative plates containing 0%, 0.005%, 0.02% and 0.04% In₂O₃, respectively.

It can be seen from the SEM images of the negative plates without In₂O₃ and with 0.005% In₂O₃, the NAM looked loose and out-of-flatness with many gas holes on the surfaces, and no large crystalline particle was observed on the electrodes. As mentioned

earlier, these two types of negative plates generated more hydrogen during the charge process, which leads to the decreased charge acceptance of the batteries. The generated hydrogen might scour the NAM, and cause the plates looser consequently. The loose electrode structure results in poor contacts between the negative electrode materials and grids to shorten the cycle life of the batteries. Moreover, the large crystalline particles on the negative plates could be PbSO₄, which were not converted to Pb even the battery was fully recharged after the cycle test. This indicates that the sulfation of the negative plates took place extensively during the cycle test, resulting in the shorter cycle life of the batteries. For the negative plate with 0.02% In₂O₃, no loose structure was

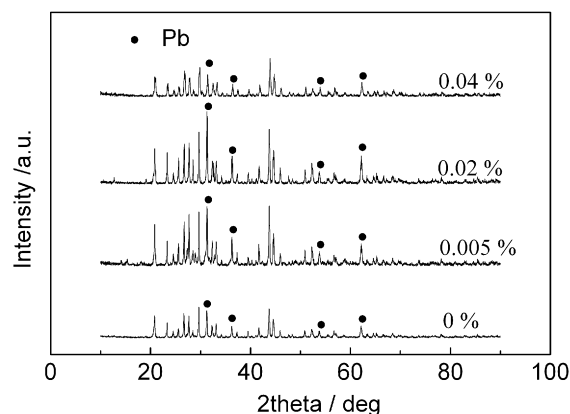


Fig. 6. XRD patterns of NAM added with different amounts of In₂O₃, after capacity recovery charging.

observed on the surface which was due to its low hydrogen evolution rate and high charge acceptance. This indicates that the electrode structure was not destroyed visibly during cycle test process. In addition, on its surface, there was no large crystalline particle. All the findings indicate that the battery added with 0.02% In_2O_3 in NAM possesses a better cycle performance. For the negative plate with 0.04% In_2O_3 , a compact surface layer of PbSO_4 was observed. The presence of compact PbSO_4 layer prevents NAM from contacting with electrolyte, and increases the polarization of the reaction of $\text{Pb} \leftrightarrow \text{PbSO}_4$. As a result, the poor cycle performance was obtained.

Fig. 6 presents the XRD patterns of NAM added with 0%, 0.005%, 0.02% and 0.04% In_2O_3 , respectively. The characteristic peaks of Pb are marked, and the other characteristic peaks are of PbSO_4 . All XRD patterns showed that there were similar characteristic peaks of Pb and PbSO_4 , but no characteristic peaks of In_2O_3 because of the too low addition amount. The intensity of the characteristic peaks of Pb and PbSO_4 varied with addition amount of In_2O_3 in NAM. It was obvious that, with increasing In_2O_3 content, the intensity of the characteristic peaks initially became increased and then decreased, e.g., the maximum relative intensity of characteristic peaks was obtained for the one with 0.02% In_2O_3 addition. It also can be seen from Fig. 6 that, when the addition amounts of In_2O_3 varied from 0% to 0.02%, the intensity of the characteristic peaks of Pb increased faster than that of PbSO_4 . This phenomenon indicates that appropriate addition of In_2O_3 in the negative plates can promote conversion of PbSO_4 to Pb in the capacity recovery process. Therefore it can be concluded that appropriate addition of In_2O_3 in the negative plates is benefit to prolong the cycle life of the battery.

4. Conclusions

1. EAC in NAM can prolong the cycle life of VRLA batteries during HRPSOC operation, whereas it may increase the evolution rate of hydrogen on the negative plates during the charge process.

2. Appropriate addition of In_2O_3 in NAM can increase the over-potential of hydrogen evolution, decrease the evolution rate of hydrogen, and prolong HRPSOC cycle life of VRLA batteries. The battery with 0.02% In_2O_3 in NAM exhibits at least four times longer cycle life than the one without In_2O_3 .
3. Appropriate addition of In_2O_3 and EAC in NAM can restrain progressive accumulation of PbSO_4 on the negative plates during the charge/discharge cycles, and promote conversion of PbSO_4 to Pb in the capacity recovery process.

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